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Quantification of Solute-Solute Interactions in Steroidal Hormone Removal by Ultrafiltration Membranes

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Abstract

Micropollutant removal by membrane filtration is variable and can be influenced by the presence of organic matter. When considering removal mechanisms, many studies have focused on membrane adsorption and solute-foulant interactions; however, little is known regarding the influence of solute-solute interactions as these are typically difficult to quantify. In this study experimental organic matter-water partition coefficients (K_{OM}) were applied to quantify and elucidate the influence of solute-solute interactions for steroidal hormone removal by ultrafiltration. The results indicated that the removal of all hormones increased in the presence of organic matter and this was related to hormone - organic matter interactions. Organic matter did not increase membrane adsorption or cause significant fouling for most molecular weight cut-off (MWCO) membranes, thus solute-solute interactions were the dominant mechanism for hormone removal as expected from previous quantification of such interactions using a specifically developed solid-phase microextraction (SPME) technique. While quantification was only partially successful at low organic carbon concentrations, clear evidence of the importance of solute-solute interactions was demonstrated in concentration studies. Experimental removal and estimated removal due to solute-solute interactions for estrone was comparable at high organic matter concentrations of 25-50 mgC/L for both 10 (48-52%) and 100 kDa (33-38%) membranes, suggesting that organic matter concentration was an important factor in solute-solute interactions. This study represents the first time that experimental organic matter-water partition coefficients have been applied to assess solute-solute interactions in membrane filtration, specifically ultrafiltration.

Keywords: Ultrafiltration, organic matter, steroidal hormone, solute-solute interaction, partition coefficient

Introduction

The detection of micropollutants, such as pharmaceuticals, pesticides and steroidal hormones, in effluent from conventional wastewater treatment plants has generated worldwide interest over the last few decades [1, 2]. This is of concern as many of these micropollutants are considered endocrine disrupting chemicals and can have implications for the growth and development of organisms. For example, the presence of steroidal hormones, such as estradiol and estrone, can cause reproductive disruption in fish at sub nanogram per litre (ng/L) concentrations [3]. Consequently, there is a need for improved micropollutant removal during water and wastewater treatment and this has led to increasing interest in advanced water treatment processes, such as membrane filtration. The removal of micropollutants by membranes is variable and the presence of organic matter, which is ubiquitous in surface and wastewaters, can affect removal [4-6]. To better understand the influence of organic matter on micropollutant removal by membrane filtration three mechanisms of interaction interplay, namely membrane adsorption, solute-foulant interactions and solute-solute interactions. For the purpose of this study, solute-foulant interactions are defined as the interaction between micropollutants and membrane foulants, while solute-solute interactions are the interaction between dissolved components such as micropollutants and organic matter.

The influence of organic matter on membrane adsorption is variable and is dependent on the properties of the micropollutant, organic matter and membrane. Studies have found decreased micropollutant adsorption in the presence of organic matter, and attributed this to competition for sorption sites [7-9]. In contrast, others have demonstrated increased micropollutant adsorption suggesting that the presence of organic matter leads to modification of the membrane, allowing for greater adsorption [10]. Jin *et al.* [5] observed the impact of different organic matter types on micropollutant adsorption behaviour. Membrane material can also have a significant influence on adsorption [11]. For example, Jermann *et al.* [12] observed up to 80% adsorption of estradiol to polyethersulfone ultrafiltration (UF) membranes compared to only 8% adsorption to regenerated cellulose UF membranes.

Solute-foulant interactions are another common mechanism for micropollutant removal, being typically indicated by flux decline. Within the literature, reports on the influence of solute-foulant interactions appear to be highly variable and dependent on properties of the micropollutant, such as charge and molecular weight, as well as organic matter properties and membrane material. Several studies have attributed improved steroidal hormone removal in the presence of organic matter to solute-foulant interactions [10, 12]. Three main mechanisms can influence micropollutant removal in fouled membranes including concentration polarisation, pore blocking and adsorption to the fouling layer [13]. Ng and Elimelech [6] studied the removal of estradiol and progesterone by reverse osmosis (RO) membranes in the presence of colloidal fouling. The results indicated that the removal of the studied hormones decreased in the presence of colloidal fouling. This was attributed to a reduction in hormone back diffusion from the membrane surface due to the fouling layer. This led to an accumulation of hormones on the membrane causing a greater concentration gradient which assisted with the diffusion of hormones across the membrane to the permeate side [6]. In contrast, several studies have also indicated increased micropollutant removal due to organic fouling. For looser nanofiltration (NF) membranes pore blocking by organic matter has been shown to reduce micropollutant transport through the membrane leading to increased removal [13]. Further, it has been suggested that the presence of the fouling layer will reduce the interaction of micropollutants with the membrane leading to a reduction in micropollutant diffusion through the membrane [14]. Plakas *et al.* [15] and McCallum *et al.* [9] observed increased micropollutant removal by NF due to the presence of organic matter suggesting that the fouling layers acted as a second barrier.

While the above two mechanisms feature prominently in the literature, other studies have suggested that the interaction of micropollutants with organic matter, otherwise known as solute-solute interactions, can lead to increased micropollutant removal [16-19]. This is because micropollutants associated with organic matter can be retained together by the membrane. However, these studies

were unable to quantify such interactions. Previous research has suggested that this interaction is influenced by organic matter type and concentration, as well as solution chemistry [20-22]. Hajibabania *et al.* [23] attempted to quantify solute-solute interactions in UF for a range of micropollutants using a mass balance approach. However, this study did not consider the influence of organic fouling for micropollutant removal by UF, which can be significant for the studied organic matter alginate [12].

Recently, several studies have applied organic matter-water partition coefficients (K_{OM}) from the literature in an attempt to quantify solute-solute interactions in membrane filtration [5, 10, 12]. K_{OM} can be used to predict micropollutant sorption to organic matter as it represents the equilibrium distribution of a micropollutant between two phases, such as organic matter and water. However, these studies applied K_{OM} values calculated for different micropollutants and at different concentrations [5, 10] or for hydrophobic membranes [12] where other mechanisms, such as membrane adsorption and fouling, dominate. By using K_{OM} values determined in the same experimental conditions as in the membrane filtration experiments, rather than literature data, it may be possible to quantify the influence of solute-solute interactions.

Consequently, the aim of this study is to quantify and hence provide evidence for the importance of solute-solute interactions for steroidal hormone removal by stirred cell UF using experimental K_{OM} values to predict hormone removal. While most studies discussed above have focused on NF or RO, UF was selected for this study to elucidate intrinsic removal of the micropollutant by the membrane due to solute-solute interactions. Given the small molecular weight of micropollutants, UF is unable to retain hormones by size exclusion; therefore, the presence of organic matter will play an important role for hormone removal. This approach is novel as it is the first study to apply experimental K_{OM} values to assess the influence of solute-solute interactions in UF.

2. Experimental

2.1 Chemicals

All chemicals were of analytical grade. The background electrolyte was 1 mM $NaHCO_3$, 20 mM NaCl and the pH was adjusted with 1 M HCl and 1 M NaOH. Purified water was used for all experiments (Elga LabWater, Marlow, UK). Radiolabelled [2,4,6,7-^{3}H]estrone (2.449 TBq/mmol) was purchased from Perkin Elmer (Beaconsfield, UK). Radiolabelled [2,4,6,7-^{3}H]17β-estradiol (3.15TBq/mmol), [1,2,6,7-^{3}H]progesterone (3.48 TBq/mmol) and [1,2,6,7-^{3}H]testosterone (2.70 TBq/mmol) were purchased from GE Healthcare (Little Chalfont, UK). All hormones have a radioactive concentration of 37 MBq/mL. Humic acid (HA) (sodium salt) was purchased from Sigma Aldrich (Gillingham, UK). The concentration of organic matter in natural waters can vary greatly, and can range from 0.2 to 30 mg of carbon per litre (mgC/L) [24, 25]. For most experiments, an organic matter concentration of 12.5 mgC/L was selected to represent natural waters, while concentrations up to 125 mgC/L were used to determine the influence of organic matter concentration for micropollutant removal. Properties of the studied hormones and HA were summarised by Neale *et al.* [26].

2.2 Membranes

Regenerated cellulose UF membranes with a polypropylene support layer were supplied by Millipore (Bedford, US). The molecular weight cut-off (MWCO) ranged from 1 to 100 kDa (determined by manufacturer). Pure water flux and estimated pore diameters for all membranes is shown in Table 1. Regenerated cellulose was selected as it is hydrophilic (contact angle 26±3° [27]) and therefore, minimal organic adsorption was expected. Prior to the experiment the membranes were soaked overnight in purified water.

[Table 1]

2.3 Ultrafiltration Stirred Cells

The experiments were conducted in stainless steel stirred cells. The volume of the cell is 990 mL with internal diameter of 70 mm giving an exposed membrane surface area of 38.48 cm^2. The maximum pressure rating of the cell was 20 bar, however, the pressure within the cell for all experiments did not exceed 5 bar due to ultrafiltration (UF) membrane pressure restrictions. The cell was pressurised using lab air which was supplied through the top of the cell. The cell contained a magnetic stirred assembly (Millipore, Watford, UK) and was stirred using a magnetic stirrer table (Fisher Scientific, Loughborough, UK) to reduce concentration polarisation. Three stainless steel cells were used in parallel for all experiments. Dead-end filtration was selected over crossflow filtration as it offered a controlled environment to study the influence of solute-solute interactions for micropollutant removal.

2.4 Filtration Protocol

A 400 mL feed solution containing 100 ng/L hormone, 12.5 to 125 mgC/L organic matter and 1 mM $NaHCO_3$ 20 mM NaCl was stirred at 200 RPM using a magnetic stirrer table for 16 h prior to the experiment to ensure equilibrium was reached. The hormone concentration was selected as it represented a realistic concentration of hormones detected in effluent impacted surface waters [28]. The solution chemistry and HA concentrations were selected to be consistent with the K_{OM} experiments. To determine hormone removal by the membrane itself, experiments were also conducted without HA. Purified water was filtered through the membrane for 30 min at 0.5 to 5 bar depending on membrane MWCO to remove the glycerine coating (Table 1). Pure water flux was measured for 60 min, with the exception of the 100 kDa membrane where only 30 min could be measured due to the high flux. Following pure water flux, a 50 mL feed sample was collected, and 350 mL was introduced to the cell. Six 50 mL permeate samples were collected during the experiment at time intervals ranging from 2 to 40 min depending on the membrane MWCO, as well as a 50 mL concentrate sample. Following the experiment, pure water flux was measured for 30 min. The membranes were cleaned by filtering with a 0.1 M NaOH solution for 30 min followed by purified water for a further 30 min. Pure water flux (J_0) was measured after cleaning to verify the absence of fouling. The membranes were stored in 0.5% $Na_2S_2O_5$ and reused up to 5 times. The flux ratio (J/J_0) was low at the beginning of all experiment and this was due to the gradual build-up of pressure in the cells.

Experimental removal ($R_{\%}$) of the hormones and organic matter by the membrane was calculated using Equation 1, where C_{P6} was the final permeate concentration and C_R was the retentate concentration. The last permeate sample was used to calculate removal as the system was closest to saturation at this point and the retentate concentration can be measured at the end of the experiment.

$$R_{\%} = (1 - \frac{C_{P6}}{C_R}) \cdot 100\% \quad \textbf{(1)}$$

As $R_{\%}$ includes removal due to adsorption, the mass adsorbed to the membrane (m) could be differentiated using Equation 2, where C was concentration (ng/L for hormones and mgC/L for HA), V was volume (L) and indices $_{F,R}$ and $_{Pi}$ indicated feed, retentate and permeate, respectively.

$$m = V_F \cdot C_F - V_R \cdot C_R - \Sigma V_{Pi} \cdot C_{Pi} \quad \textbf{(2)}$$

Mass adsorbed can also be expressed as percent mass adsorbed of total mass available from the feed solution ($m_{\%}$) (Equation 3).

$$m_{\%} = (\frac{m}{C_F \cdot V_F}) \cdot 100\% \quad \textbf{(3)}$$

2.5 Analytical Methods

1 mL of the feed, permeate and concentrate samples were analysed in 20 mL glass scintillation vials containing 7 mL of Ultima Gold LLT liquid scintillation (Beaconsfield, UK). The activity of the

samples was counted in triplicate using a Beckman LS 6500 liquid scintillation counter (Fullerton, USA). The HA concentration in the feed, permeate and concentrate samples was measured using a total organic carbon (TOC-V CPH) analyser in non-purgeable organic carbon (NPOC) mode (Shimadzu, Milton Keyes, UK).

The variation associated with removal and adsorption was determined by considering the pure water flux variability. Pure water flux was selected as it varied more between experiments under the same conditions than other experimental parameters, such as temperature and concentration measurements. The differences between flux and removal were determined using two repeated experiments which allowed a linear relationship between flux and removal to be established. By applying the total difference in flux to the linear relationship the relative variation associated with hormone removal was estimated to be 5.3%.

2.6 Organic matter-water partitioning

Organic matter-water partition coefficients, K_{OM} (L/kg), were estimated using a mass balance form of solid-phase microextraction (SPME). The methodology used has been described in detail elsewhere [29]. Using experimental K_{OM} values the anticipated hormone removal due to solute-solute interactions could be estimated. Firstly, the fraction of hormone partitioned to organic matter, f_{OM} (%), was determined using Equation 4 where V_W was the volume of aqueous solution (L) and m_{HA} was the total mass of HA in solution (kg).

$$f_{OM} = \frac{1}{\frac{V_W}{(m_{HA} \cdot K_{OM})} + 1} \quad \textbf{(4)}$$

Using f_{OM} it was possible to estimate hormone removal due to solute-solute interactions ($R_{E\%}$) using Equation 5 where $R_{OM\%}$ was experimental organic matter removal (%). Despite the difference in equilibrium time for the stirred cell (16 h) and K_{OM} experiments (24 h) this comparison was still applicable as method development for the stirred cell experiments indicated that there was no significant difference between observed removal at 16 and 24 h.

$$R_{E\%} = f_{OM} \cdot R_{OM\%} \quad \textbf{(5)}$$

3. Results and Discussion

3.1 Hormone Removal by UF

Minimal removal of steroidal hormones by UF in the absence of organic matter was anticipated due to the small size of the hormones relative to the membrane pore size, 0.8-0.9 nm and 1.6-18.2 nm, respectively. However, up to 28% removal is observed in Figure 1A, with removal increasing with decreasing membrane MWCO. Removal was related to membrane adsorption (Figure 2), with greater removal by lower MWCO membranes due to longer experiment duration. Variable removal of steroidal hormones in the absence of organic matter has been observed previously for UF and was related to mass adsorption [30]. There was no correlation between adsorption and hydrophobicity, as indicated by octanol-water partition coefficients (log K_{OW}). Further, adsorption was not influenced by charge, with all hormones are predominantly neutral at the studied pH. Instead, progesterone sorbed significantly more than the other studied hormones as it is less polar due to its lack of bipolar functional groups. Consequently, it is less likely to stay in aqueous solution and instead sorbs to a solid phase. This indicates the importance of micropollutant physio-chemical properties, such as functional group content, when considering micropollutant removal by membrane filtration.

[Figure 1]

[Figure 2]

3.2 Influence of Organic Matter on Hormone Removal by UF

The presence of organic matter was expected to increase steroidal hormone removal due to solute-solute interactions as experimental K_{OM} values in Table 2 indicate that the studied hormones interact with organic matter. Increased removal in the presence of organic matter was observed for all hormones (Figure 1B) and was related to organic matter removal (Figure 3). As a result, decreased hormone removal with increasing membrane MWCO was related to decreased organic matter removal. Yoon *et al.* [31] also observed increased hormone removal by UF in the presence of organic matter. The significantly higher removal of progesterone compared to the other hormones was related to its affinity for organic matter as indicated by the experimental log K_{OM} values (Table 2), as well as significant adsorption to the membrane as discussed above. Within the literature, many studies have quantified the interaction of estradiol with natural organic matter (NOM), though there have not been as many studies for the other hormones. The K_{OM} value for estradiol is similar to literature K_{OM} values measured for Aldrich HA [32, 33].

[Table 2]

[Figure 3]

To elucidate the mechanisms of micropollutant removal in the presence of organic matter, the influence of membrane adsorption, solute-foulant interactions and solute-solute interactions were differentiated. The presence of organic matter did not have a significant influence on micropollutant adsorption (Figure 2). Many studies have found decreased hormone adsorption in the presence of organic matter due to competition for membrane surface sites [7-9], while Hu *et al.* [10] found increased adsorption of estrone with HA using polyamide and cellulose acetate NF membranes. The lack of difference may be related to the use of hydrophilic membranes in the present study, as well as the low hormone concentration. Jermann *et al.* [12] compared estradiol adsorption to hydrophobic and hydrophilic UF membranes in the presence of organic matter and found no difference in adsorption with organic matter for hydrophilic membranes. As adsorption is a dynamic equilibrium, adsorption to the membrane in the absence and presence of organic matter may differ with longer experiment times.

Flux decline, which is an indicator of fouling, was only observed for the large MWCO membranes (Table 1). Jermann *et al.* [12] suggested that organic matter fouling was the dominant cause of micropollutant removal in UF in the presence of HA. Several other studies have indicated the importance for organic matter fouling for micropollutant removal in NF [15, 34, 35]. While it is possible that solute-foulant interactions contribute to hormone removal for the 30 and 100 kDa membranes, no flux decline was observed for the 1 to 10 kDa membranes thus excluding this mechanism for those membranes. HA sorption to the membrane was measured using a mass balance approach and this varied from 1 to 13% (0.001-0.007 mg/cm2); however, as such variation is within experimental error, no variation with MWCO could be established. Similar flux decline in the presence of HA was observed by Yuan and Zydney [36] for larger MWCO membranes. This study indicated that the dominant fouling mechanism was HA deposition leading to pore blocking, rather than concentration polarisation or membrane adsorption, due to the large molecular weight of the studied HA. Increased organic matter removal due to pore blocking has been observed in the literature [37]. Therefore, if pore blocking was the dominant cause of micropollutant removal in this study then greater removal would be expected with increasing membrane MWCO, however, Figure 3 indicates that the opposite is the case. In fact, the flux ratio was slightly above 1 for 1-5 kDa membranes; however, this is most likely due to the presence of salts and organic matter rendering the membranes more hydrophilic [38].

As the presence of organic matter did not increase membrane adsorption or cause significant fouling given our experimental design, solute-solute interactions were expected to mainly contribute to steroidal hormone removal. Figure 3 indicates limited similarity between $R_{\%}$ and $R_{E\%}$ for the studied hormones. For estradiol, progesterone and testosterone there was some comparison between $R_{\%}$ and $R_{E\%}$ for high MWCO membranes, but generally $R_{E\%}$ was significantly lower than $R_{\%}$. In

contrast, there was only similarity between $R_{E\%}$ and $R_{\%}$ for estrone at the 1 kDa membrane, with removal due to solute-solute interactions overestimated for higher MWCO membranes. Permeation of some smaller HA fractions may affect prediction of solute-solute interactions, however, this is unlikely to influence the 1-10 kDa membranes where high removal of HA (≥95%) was observed.

Previous studies have observed that organic matter concentration controls sorption of micropollutants in membrane filtration [19] and natural systems [39]. Consequently, the studied organic matter concentration (12.5 mgC/L) may be too low to estimate partitioning accurately. Therefore, a study of higher organic matter concentrations was performed.

3.3 Influence of Organic Matter Concentration on Estrone Removal

An increase in organic matter concentration was expected to increase estrone removal due to greater partitioning with the higher organic matter mass. Only estrone was selected for this study as it showed limited membrane sorption yet still interacted strongly with HA (Table 2). Indeed, Figure 4 indicates increasing estrone removal as organic matter concentration increases from 12.5 to 125 mgC/L for both 10 and 100 kDa membranes.

[Figure 4]

Increased removal as a function of organic matter concentration has been observed previously in the literature with Dalton *et al.* [19] finding increased micropollutant removal at high organic matter to micropollutant ratios. Agbekodo *et al.* [21] also observed greater pesticide removal by NF at higher organic matter concentrations and this was attributed to increased micropollutant adsorption on the membrane with increasing organic matter concentration. This was not the case in the present study as the increasing organic matter concentration did not significantly alter estrone adsorption to the membrane with 6.2% adsorption at 12.5 mgC/L compared to 5.5% adsorption at 125 mgC/L for the 100 kDa membrane.

Ghaemi *et al*. [40] found increased p-nitrophenol removal during UF as organic matter concentration increased in the cell and attributed this to the formation of a cake deposit on the membrane. To determine if solute-foulant interactions contributed to micropollutant removal with increasing organic matter concentration flux decline was assessed (Figure 5). No flux decline for the 10 kDa membrane was observed, but up to 60% decline in flux at 125 mgC/L was observed for the 100 kDa membrane. This was confirmed by an increase in HA adsorption/deposition at 125 mgC/L (19% compared to 6-9% at 12.5-50 mgC/L). The higher HA concentrations were expected to increase pore blocking of the 100 kDa membrane, which makes it difficult to separate solute-solute interactions from solute-fouling interactions. Despite the lack of flux decline for the 10 kDa membrane, the mass balance suggested significant adsorption/deposition of HA to the membrane at the 125 mgC/L concentration (0.7 mg/cm^2 or 64% adsorption). Therefore, solute-foulant interactions cannot be excluded from the estrone removal mechanisms for the 10 kDa membrane.

[Figure 5]

Using experimental K_{OM} values to estimate hormone removal due to solute-solute interactions (Table 2) $R_{\%}$ and $R_{E\%}$ were only similar at higher organic matter concentrations (25 and 50 mgC/L) for both 10 and 100 kDa membranes (Figure 6). At 125 mgC/L $R_{E\%}$ was lower than $R_{\%}$ for both 10 and 100 kDa membranes, but this may be related to the solute-foulant interactions as discussed above. The correspondence between $R_{\%}$ and $R_{E\%}$ at 25 and 50 mgC/L suggested that the increasing organic matter concentration led to more measurable estrone partitioning which increased removal, confirming that organic matter concentration was the limiting factor in solute-solute interactions. This was also hypothesized by Dalton *et al.* [19], though this study was not able to provide evidence of solute-solute interactions. While estimating hormone removal using K_{OM} values currently has some limitations as low organic matter concentrations and membrane fouling can impair predictions, this study represents the first occasion that the importance of solute-solute interactions for micropollutant removal has been demonstrated for UF.

[Figure 6]

4. Conclusions

The importance of solute-solute interactions for micropollutant removal in membrane filtration has been hypothesised in the last decade, with studies recently applying literature K_{OM} values to assess this interaction [10, 12]. By systematically separating contributions of membrane adsorption, solute-foulant interactions and experimentally determined K_{OM} values, this research was able to quantify and provide evidence of the impact of solute-solute interactions in ultrafiltration (UF). While the quantification was only partially successful at low organic matter concentrations, clear evidence of the importance of solute-solute interactions was demonstrated when concentration of organic matter was studied. This suggests the organic matter concentration is the determining factor in solute-solute interactions and relates to micropollutant removal.

While UF would not be applied to remove micropollutants alone, it can be used as a pre-treatment step prior NF or RO or as a separation stage in a membrane bioreactor (MBR) or hybrid process, such as powdered activated carbon-UF. For example, Kovalova et al. [41] found variable removal of a range of micropollutants in hospital wastewater using MBR with UF membranes. The dissolved organic carbon concentration in the wastewater was as high as 120 mgC/L, thus it is possible that solute-solute interactions contributed to removal, though this was not explored in their study. This emphasises the importance of understanding solute-solute interactions in membrane filtration and the current paper provides the methodology to quantify such interactions.

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Nomenclature

C_F	Feed concentration (ng/L for hormones and mgC/L for humic acid)
C_P	Permeate concentration (ng/L for hormones and mgC/L for humic acid)
C_R	Retentate concentration (ng/L for hormones and mgC/L for humic acid)
f_{OM}	Fraction of hormone partitioned to organic matter at equilibrium (%)
J	Flux (L/m^2.hr)
J_0	Pure water flux (L/m^2.hr)
K_{OM}	Organic matter-water partition coefficient (L/kg)
m	Mass adsorbed to the membrane (ng for hormones and mg for humic acid)
$m_{\%}$	Percent mass adsorbed in the feed solution (%)
m_{HA}	Total mass of humic acid in solution (kg)
$R_{\%}$	Experimental hormone removal (%)
$R_{E\%}$	Estimated hormone removal due to solute-solute interactions (%)
$R_{OM\%}$	Experimental organic matter removal (%)
V_F	Feed volume (L)
V_P	Permeate volume (L)
V_R	Retentate volume (L)
V_W	Volume of aqueous solution (SPME experiment) (L)

References

[1] T.A. Ternes, Occurance of drugs in German sewage treatment plants and rivers, Water Res., 32 (1998) 3245-3260.

[2] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data, Toxicology Letters, 131 (2002) 5-17.

[3] A.M. Vajda, L.B. Barber, J.L. Gray, E.M. Lopez, J.D. Woodling, D.O. Norris, Reproductive disruption in fish downstream from an estrogenic wastewater effluent, Environ. Sci. Technol., 42 (2008) 3407-3414.

[4] E.C. Devitt, M.R. Wiesner, Dialysis investigations of atrazine-organic matter interactions and the role of a divalent metal, Environ. Sci. Technol., 32 (1998) 232-237.

[5] X. Jin, J. Hu, S.L. Ong, Influence of dissolved organic matter on estrone removal by NF membranes and the role of their structures, J. Membr. Sci., 41 (2007) 3077-3088.

[6] H.Y. Ng, M. Elimelech, Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis, J. Membr. Sci., 244 (2004) 215-226.

[7] S. Chang, T.D. Waite, A.I. Schäfer, A.G. Fane, Adsorption of the endocrine-active compound estrone on microfiltration hollow fiber membranes, Environ. Sci. Technol., 37 (2003) 3158-3163.

[8] A.M. Comerton, R.C. Andrews, D.M. Bagley, P. Yang, Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds, J. Membr. Sci., 303 (2007) 267-277.

[9] E.A. McCallum, H. Hyung, T.A. Do, C.-H. Huang, J.-H. Kim, Adsorption, desorption, and steady-state removal of 17β-estradiol by nanofiltration membranes, J. Membr. Sci., 319 (2008) 38-43.

[10] J.Y. Hu, X. Jin, S.L. Ong, Rejection of estrone by nanofiltration: Influence of solution chemistry, J. Membr. Sci., 302 (2007) 188-196.

[11] A.I. Schafer, I. Akanyeti, A.J.C. Semiao, Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens, Advances in Colloid and Interface Science, 164 (2011) 100-117.

[12] D. Jermann, W. Pronk, M. Boller, A.I. Schäfer, The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration, J. Membr. Sci., 329 (2009) 75-84.

[13] L.D. Nghiem, S. Hawkes, Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size, Separation and Purification Technology, 57 (2007) 176-184.

[14] L.D. Nghiem, D. Vogel, S. Khan, Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator, Water Res., 42 (2008) 4049-4058.

[15] K.V. Plakas, A.J. Karabelas, T. Wintgens, T. Melin, A study of selected herbicides retention by nanofiltration membranes -the role of organic fouling, J. Membr. Sci., 284 (2006) 291-300.

[16] X. Jin, J.Y. Hu, S.L. Ong, Removal of natural hormone estrone from secondary effluents using nanofiltration and reverse osmosis, Water Res., 44 (2010) 638-648.

[17] E.C. Devitt, F. Ducellier, P. Cote, M.R. Wiesner, Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure-driven membranes, Water Res., 32 (1998) 2563-2568.

[18] A.I. Schäfer, L.D. Nghiem, N. Oschmann, Bisphenol A retention in the direct ultrafiltration of greywater, J. Membr. Sci., 283 (2006) 233-243.

[19] S.K. Dalton, J.A. Brant, M.R. Wiesner, Chemical interactions between dissolved organic matter and low-molecular weight organic compounds: Impacts on membrane separation, J. Membr. Sci., 266 (2005) 30-39.

[20] L.D. Nghiem, A. Manis, K. Soldenhoff, A.I. Schäfer, Estrogenic hormone removal from wastewater using NF/RO membranes, J. Membr. Sci., 242 (2004) 37-45.

[21] K.M. Agbekodo, B. Legube, S. Dard, Atrazine and simazine removal mechanisms by nanofiltration: Influences of natural organic matter concentration, Water Res., 30 (1996) 2535-2542.

[22] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Nanofiltration of hormone mimicking trace organic contaminants, Separation Science and Technology, 40 (2005) 2633-2649.

[23] S. Hajibabania, A. Verliefde, J.A. McDonald, S.J. Khan, P. Le-Clech, Fate of trace organic compounds during treatment by nanofiltration, J. Membr. Sci., 373 (2011) 130-139.

[24] F.H. Frimmel, G. Abbt-Braun, Basic characterization of reference NOM from Central Europe-similarities and differences, Environ. Int., 25 (1999) 191-207.

[25] E.T. Gjessing, P.K. Egeberg, J. Håkedal, Natural organic matter in drinking water-the 'NOM-typing project', background and basic characteristics of original water sample and NOM isolates, Environ. Int., 25 (1999) 145-159.

[26] P.A. Neale, B.I. Escher, A.I. Schäfer, pH dependence of steroid hormone-organic matter interactions at environmental concentrations, Sci. Total Environ., 407 (2009) 1164-1173.

[27] J. Pieracci, J.V. Crivello, G. Belfort, Photochemical modification of 10 kDa polyethersulfone ultrafiltration membranes for reduction of biofouling, J. Membr. Sci., 156 (1999) 223-240.

[28] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance, Environ. Sci. Technol., 36 (2002) 1202-1211.

[29] P.A. Neale, B.I. Escher, A.I. Schäfer, Quantification of solute-solute interactions using negligible-depletion solid-phase microextraction: Measuring the affinity of estradiol to bulk organic matter, Environ. Sci. Technol., 42 (2008) 2886-2892.

[30] Y. Yoon, P. Westerhoff, S. Snyder, E. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci., 270 (2006) 88-100.

[31] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination, 202 (2007) 16-23.

[32] H. Yamamoto, H.M. Liljestrand, Y. Shimizu, M. Morita, Effects of physical-chemical characteristics on the sorption of selected endocrine disruptors by dissolved organic matter surrogates, Environ. Sci. Technol., 37 (2003) 2646-2657.

[33] X. Qiao, N. Carmosini, F. Li, L.S. Lee, Probing the primary mechanisms affecting the environmental distribution of estrogen and androgen isomers, Environ. Sci. Technol., 45 (2011) 3989-3995.

[34] P. Xu, J.E. Drewes, T.-U. Kim, C. Bellona, G. Amy, Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, J. Membr. Sci., 279 (2006) 165-175.

[35] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, I. Petrinic, T. Luxbacher, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Influence of membrane fouling by (pretreated) surface water on rejection of pharmaceutically active compounds (PhACs) by nanofiltration membranes, J. Membr. Sci., 330 (2009) 90-103.

[36] W. Yuan, A.L. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol., 34 (2000) 5043-5050.

[37] E. Aoustin, A.I. Schäfer, A.G. Fane, T.D. Waite, Ultrafiltration of natural organic matter, Separation and Purification Technology, 22-23 (2001) 63- 78.

[38] A.I. Schäfer, L.D. Nghiem, A. Meier, P.A. Neale, Impact of organic matrix compounds on the retention of steroid hormone estrone by a 'loose' nanofiltration membrane, Separation and Purification Technology, 73 (2010) 179-187.

[39] A.C. Johnson, C. White, T.J. Besien, M.D. Jürgens, The sorption potential of octylphenol, a xenobiotic oestrogen, to suspended and bed-sediments collected from industrial and rural reaches of three English rivers, Sci. Tot. Environ., 210-211 (1998) 271-282.

[40] N. Ghaemi, S.S. Madaeni, M. De Nobili, A. Alizadeh, Ultrafiltration behavior of nitrophenols in the presence of humic substances, J. Membr. Sci., 331 (2009) 126-136.

[41] L. Kovalova, H. Siegrist, H. Singer, A. Wittmer, C.S. McArdell, Hospital wastewater treatment by membrane bioreactor: Performance and efficiency for organic micropollutant elimination, Environ. Sci. Technol., (2012) In press.

[42] A.I. Schäfer, Natural Organics Removal Using Membranes: Principles, Performance, and Cost, CRC Press, Boca Raton, 2001.

[43] E. Worch, Eine neue gleichung zur berechnung von diffusionskoeffizienten gelöster stoffe, Vom Wasser, 81 (1993) 289-297.

Tables

Table 1: Key properties of the ultrafiltration membranes used

Membrane Type	MWCO (kDa)	Pore Diameter* (nm)	Pressure (Bar)	Pure Water Flux ($L/m^2.h$)	Final Flux† ($L/m^2.h$)	Flux Ratio (-)
PLAC	1	1.6	5	20.8	21.9	1.1
PLBC	3	2.8	5	30.0	31.1	1.0
PLCC	5	3.7	5	53.0	54.3	1.0
PLGC	10	5.4	5	89.4	87.8	0.1
PLTK	30	9.6	1	296.7	268.9	0.9
PLHK	100	18.2	0.5	359.2	288.5	0.8

*Pore diameter was estimated using an equation adapted by Schäfer [42] based on the Stokes-Einstein equation and a diffusion constant equation from Worch [43]

†1 mM $NaHCO_3$, 29 mM NaCl, pH 8, 12.5 mgC/L HA

Table 2: Experimental organic matter-water partition coefficients (log K_{OM}) and estimated fraction partitioned to organic matter (f_{OM}) as a function of hormone type (12.5 mgC/L HA) and organic matter concentration (estrone only) (1 mM $NaHCO_3$, 20 mM NaCl, pH 8, 100 ng/L hormone)

	log K_{OM} (L/kg) ± variance	Estimated fraction partitioned to organic matter (f_{OM}) (%)[a]
Function of hormone type		
Estradiol	4.24 ± 0.25	17.85%
Estrone	4.86 ± <0.01	47.36%
Progesterone	4.59 ± 0.10	32.47%
Testosterone	4.04 ± 0.21	11.99%
Function of humic acid concentration (mgC/L)		
12.5	4.86 ± <0.01	47.36%
25	4.63 ± 0.01	51.43%
50	4.39 ± 0.01	54.88%
125	4.13 ± 0.03	63.03%

Figures

Figure 1: Experimental hormone removal ($R_{\%}$) in the A) absence and B) presence of organic matter as a function of membrane MWCO (1 mM $NaHCO_3$, 20 mM NaCl, pH 8, 100 ng/L hormone, 12.5 mgC/L HA)

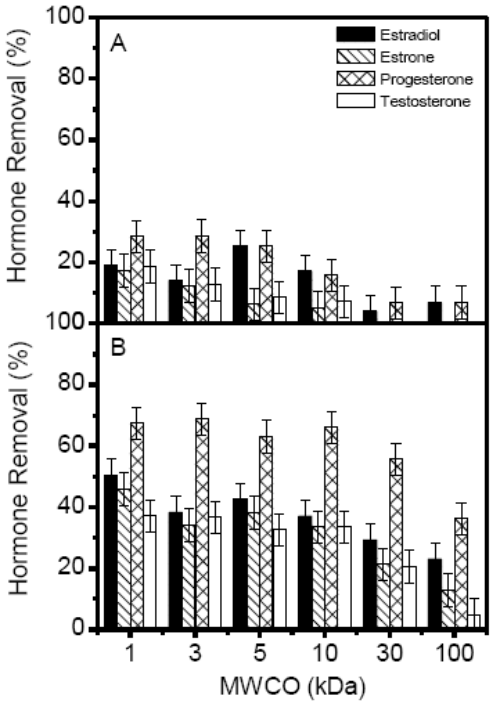

Figure 2: Hormone mass adsorbed to the membrane ($m_{\%}$) as a function of membrane MWCO for A) estradiol, B) estrone, C) progesterone and D) testosterone (Same conditions as Figure 1)

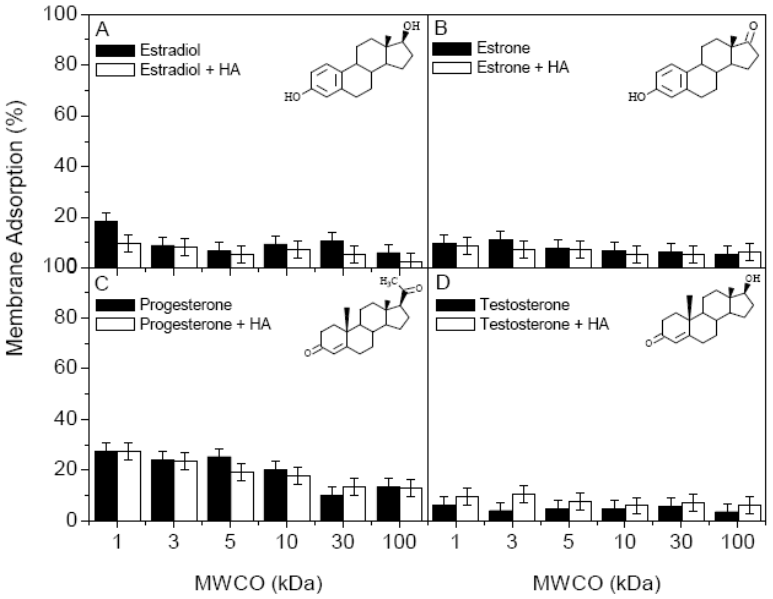

Figure 3: Estimated hormone removal ($R_{E\%}$) using experimental organic matter-water partition coefficients (log K_{OM}) and experimental hormone removal ($R_{\%}$) with organic matter removal ($R_{OM\%}$) as a function of membrane MWCO for A) estradiol, B) estrone, C) progesterone and D) testosterone (Same conditions as Figure 1)

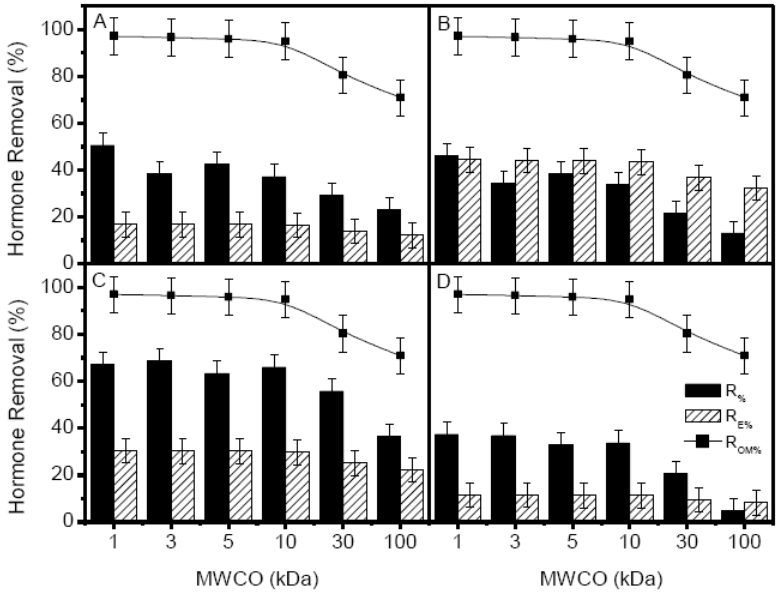

Figure 4: Experimental estrone removal ($R_{\%}$) for 10 and 100 kDa MWCO membranes as a function of HA concentration (1 mM $NaHCO_3$, 20 mM NaCl, pH 8, 100 ng/L estrone, HA concentrations of 0, 12.5, 25, 50 and 125 mgC/L)

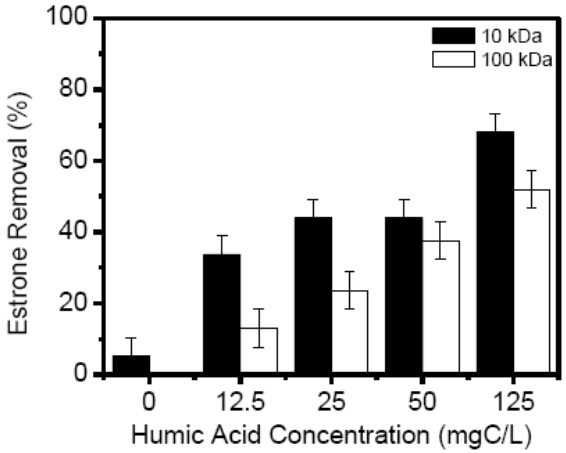

Figure 5: Flux decline as a function of HA concentration for A) 10 kDa and B) 100 kDa MWCO membranes (Same conditions as Figure 4)

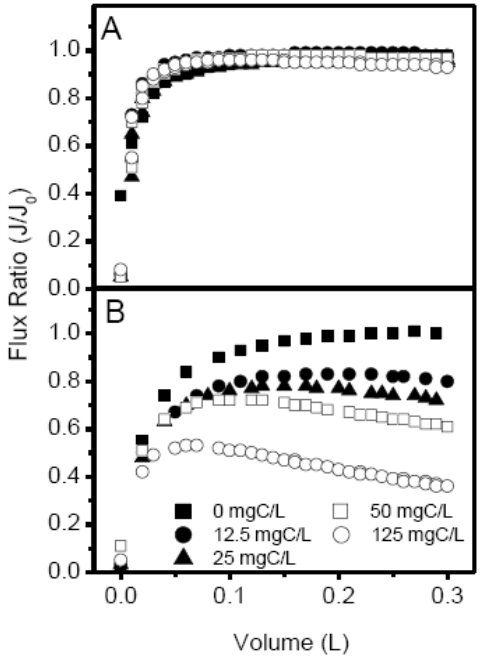

Figure 6: Estimated estrone removal ($R_{E\%}$) using experimental organic matter-water partition coefficients (log K_{OM}) and experimental hormone removal ($R_{\%}$) with organic matter removal ($R_{OM\%}$) as a function of organic matter concentration for A) 10 kDa and B) 100 kDa (Same conditions as Figure 4)